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# CANADIAN PATENT

MANUFACTURE OF CELLULOSIC PRODUCT

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Granted to Kimberly-Clark Corporation, Neenah, Wisconsin,  
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This invention relates to cross-linked cellulose fiber products and to a method of producing the same from cellulose fibers and particularly those cellulosic fibers which are capable of being formed into a paper sheet. Such fibers are termed herein "papermaking fibers."

It has now been discovered that cellulose fiber, when impregnated with a cross-linking agent and subjected to a cross-linking reaction while the fiber is in a substantially nonswollen, loosely fluffed condition, achieves very desirable modification of the fiber for many applications. Thus, the modified fiber produced in accordance with the invention attains a unique balance of hydrophobic and hydrophilic properties, in contrast to the very generally predominant hydrophilic characteristic of the initial or starting fiber.

Characteristics imparted to cellulose fiber produced in the practice of the invention include: a very materially lowered expansivity of the fiber with moisture pickup over a wide range of relative humidities; a lowered moisture regain, particularly in the higher humidity ranges; additionally, and of prime importance, these new fibers in loose mass form have a high bulk and resiliency in both the dry and wet state as compared with the initial or starting fibers from which they are produced. A mass of the new fibers in loose mat form has a low resistance to fluid flow yet exhibits a high capacity for fluid retention without material physical distortion of the fiber mass, but such mass is nevertheless readily dewatered. The new fibers themselves have little affinity for each other in the wet or dry state and display substantially no interfiber bonding capacity but yet a mass of the fibers exhibits a high wicking rate and high absorbercy

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for polar liquids. The fibers also retain the natural shape of the original fibers which, for wood fibers, is usually a somewhat kinked or coil shape, but the fibers are more rigid, even when wetted, and are less deformable under load. The rigidity of the new fibers, while not such as to render a fiber mass brittle, is such that the fibers may not be refined or beaten in conventional pulping processes without powdering of the fibers. Yet the fibers themselves are highly dispersible in aqueous media and form water-laid webs of exceptional formation and uniformity despite their low degree of hydration; such webs also are readily dried free of water and are not readily plasticized by water, as indicated by the qualities of high wet stiffness, high wet bulk and porosity, high wet resiliency, low dry density in fluff form, and low wet compressibility under light loads.

These mentioned diverse characteristics of the fiber products render the fiber material useful in a plurality of fields - as absorbents in sanitary applications, as filters for fluids, as furnish components for saturating papers, and as cushioning materials and wipes, for example.

It is accordingly a primary object of the present invention to provide cellulose fibers having novel properties.

It is also an important object of the invention to provide novel methods for the production of such fibers.

It is a further object of the invention to provide cellulose fiber products of new and improved properties.

Papermaking fibers which serve as the basis for the production of the new fibers include wood pulp fibers, hemp fiber, short cotton fibers, alpha cellulose, cotton linters, short-cut regenerated cellulose fibers, and the like. The

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wood pulp may be sulfate, sulfite, or groundwood, bleached or unbleached. Such fibers have a natural form, wood pulp fibers, for example, having a slight kink or curl which is retained in the product and which persists even when the fiber is wetted, thus contributing to the bulk and resiliency of a mat or mass of the fibers; the characteristics of such mat or mass are further enhanced by the improved rigidity of the cross-linked fiber. Additionally, these papermaking fibers are free, that is, unbeaten, are all relatively short and are

10 readily interfelted with themselves to form a sheet although the cross-linked product fibers of the same length range have so little affinity for each other that a bonding agent - such as a synthetic resin - is required to attain a strong, coherent sheet structure.

The free papermaking fibers, bleached or unbleached, in the process of the invention are first impregnated or padded with a cross-linking agent and a catalyst. Such cross-linking agents are in themselves well known, they apparently function to link cellulose molecules together, the

20 cross-links acting to provide a rigid molecular structure which sets the fiber form to a degree. Formaldehyde, dimethylol urea, and other known cross-linking agents serve the purpose well; however, formaldehyde is generally less expensive and fully effective at low levels of reaction. The impregnation is effected while the fiber is expanded or swollen, thus insuring entry of the cross-linking agent and catalyst in quantity to the fiber interior. Bleached pulp is

30 preferred as such responds more rapidly to the cross-linking action; the catalyst, which is most suitably acidic, may include any kind of acid compatible with the impregnant and which does not cause material cellulose degradation.

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The wetted impregnated fiber, usually in sheet or matted form, is dried substantially free of water prior to the cross-linking reaction between the impregnant and the cellulose molecules; such drying may precede or accompany a defibering of the sheet or mat. This defibering is sufficient to insure that the fiber is in fluff form and that contact between fibers is minimal but fiber cutting and fiber damage to any material extent should be avoided. The presence of moisture to the extent of about 10-15% based on the dry weight of the  
10 fibers aids the mechanical separation while providing assurance against fiber injury. Thus, the reaction is carried out while the dry fibers are in substantially individual or loosely associated state, a factor which inhibits cross-linking between fibers and promotes cross-linking of molecules within a fiber, thus avoiding hard fiber clump formation. In effect, the fibers are set by the cross-linking action in their generally natural fluff condition and while a minimum of cohesive force exists between fibers.

The temperature of the cross-linking reaction is  
20 dependent to some extent upon the nature of the cellulose undergoing reaction; for wood pulp fibers the temperature range is between 110-165°C.

The fiber configuration is substantially unchanged by the process. Further, and most importantly, the fiber retains its ability to wet-form, that is, the fiber may be water-laid and then dried to a fluff. In such fluff form the fiber finds particular utility in absorbent and filter applications.

Specifically, the water-holding capacity and wet  
30 bulk, particularly under mild compression loads, of the

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cross-linked fiber fluff has been found to be very materially greater and even double that of the untreated cellulosic fluff; the wicking rate of the cross-linked material in compressed form is also disproportionate, being significantly higher than that of the fluff from which it is derived. These two factors provide for particular interest in product formation.

10 However, unlike a mass of original untreated cellulose fibers wherein water is retained by the swollen flexible walls of the fibers and in the pores of the mass, the retention with a fiber mass of the invention is substantially entirely within relatively large capillary voids formed between stiffened fibers. Thus, the water retained by a mass of the stiffened fibers of the invention is readily displaced by other fluids such as air (suction pressure), and the fiber is readily dried even by blotting. So also a fiber mass which includes fibers produced in accordance with the invention is susceptible to rapid dewatering as in sheet formation and sheet drying on a paper machine. In contrast thereto, fibers of the mass of untreated fibers are relatively flexible and  
20 when subjected to pressure to expel or withdraw water from the mass, the fibers themselves compact, tending to close the pores and to thereby inhibit water withdrawal.

Also, such dewatered fiber mat or sheet exhibits a desirable resiliency for the purpose and the fibers are not compacted together as they would be were the original untreated cellulose fibers employed in the mat.

The following Table I indicates the absorbent capacity of fluff masses of the fiber produced in accordance with the invention relative to the original pulp. In the table the  
30 untreated pulp is so designated; Examples 1 to 10 inclusive are specifically described hereinafter.

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Table I

Absorbent Capacity Relative to Untreated  
Pulp at Different Compressive Loads

		<u>Relative Absorbency Under the Following Compressions</u>			
<u>Pulp Reference</u>		<u>0.0</u>	<u>0.5</u>	<u>1.0</u>	<u>2.0 psi</u>
	Untreated Pulp	1.0	1.0	1.0	1.0
	Example 1	1.2	1.8	1.8	1.8
	Example 2	1.3	2.0	2.0	1.9
10	Example 3	1.4	1.8	1.8	1.7
	Example 4	1.4	1.7	1.7	1.6
	Example 5	1.1	1.7	1.8	1.8
	Example 6	1.1	1.6	1.7	1.7
	Example 7	1.4	2.0	2.0	1.9
	Example 8	1.3	1.8	1.8	1.8-
	Example 9	1.4	1.9	1.8	1.7
	Example 10	1.1	1.3	1.3	1.3

The change in wet pad thickness occasioned by the treatment of invention is illustrated in Table II by comparison of the wet untreated pulp pad with pads produced from the cross-linked pulps of Examples 1-10; the comparison is under light compressive loadings. As may be readily seen from the table, the pad thickness is greater and, particularly, materially greater for the product of Examples 1-9.

Table II

Pad Thickness (Wet) Relative to Untreated  
Pulp at Different Compressive Loads

		<u>Relative Wet Thickness Under the Following Compressions</u>		
<u>Pulp Reference</u>		<u>0.5</u>	<u>1.0</u>	<u>2.0 psi</u>
	Untreated Pulp	1.0	1.0	1.0
30	Example 1	1.8	1.6	1.6



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	Relative Wet Thickness under the Following Compressions		
Example 2	2.0	1.8	1.7
Example 3	1.8	1.6	1.6
Example 4	1.7	1.6	1.5
Example 5	1.6	1.6	1.5
Example 6	1.6	1.5	1.5
Example 7	1.9	1.8	1.7
Example 8	1.8	1.7	1.7
10 Example 9	1.9	1.7	1.6
Example 10	1.3	1.2	1.2

The mode of attainment of the specific comparative data of Tables I and II is described in connection with Example 1 set out hereinafter.

The invention will be more fully understood from the following detailed examples and the accompanying drawings wherein:

Fig. 1 is a graph illustrating the specific filtration resistance of the cross-linked fibers of the invention with relation to untreated fibers;

Fig. 2 is a graph comparing the compressibility or wet bulk of the treated and untreated fibers;

Fig. 3 is a comparative illustration of:

a) a mass of dry fibers in accordance with the invention;

b) a mass of fibers similar to those in a) but containing 30% of water based on a dry basis weight; and

c) a pad of untreated fiber in the dry state.

Fig. 4 is a graph indicating the effect of humidity conditions on moisture pickup of the untreated versus treated fibers; and

Fig. 5 illustrates a sheet formed of a composite mass of fibers including fibers of the invention.

Example 1

About 30 grams of an unbeaten, bleached southern pine kraft pulp was made up in the form of a hand sheet to a thickness of about 0.010". This sheet was presaturated at room temperature with a formalin solution containing 37% formaldehyde and 5 grams per liter of aluminum sulfate as catalyst; presaturation was achieved by immersing the sheet  
10 in a bath of the liquid for about one minute, which materially swelled the fibers and permitted penetration of the formaldehyde and catalyst into the fiber structure. The sheet, upon removal from the bath, was drained and pressed on a blotter to a consistency of 1 part fiber to 2 parts by weight of solution. The sheet was then air dried to a moisture content of about 10-12% and thereafter defibered. Retention of some moisture in the fiber at this stage aids defibering. The defibering relaxes the fibers and prevents the intimate contact normally accompanying simple drying. This defibering  
20 was effected in a bath of carbon tetrachloride in a Waring blender at low speed to avoid fiber damage. The resulting fiber, upon removal from the blender, was dried free of the carbon tetrachloride and then introduced into a vacuum desiccator and dried of the remaining moisture at room temperature over night under reduced pressure in the presence of solid paraformaldehyde and with barium oxide present as a desiccant. The paraformaldehyde produces a vapor phase which inhibits formaldehyde evaporation during the drying. The fiber at this time is in the form of a fluff achieved by  
30 the mild agitation and the cross-linking action has not yet

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taken place. The fluff has a generally white cottony appearance and has a multiplicity of relatively large interconnecting voids. This desiccator treatment removed substantially all moisture and collapsed the fibers to essentially the physical condition of the original dry pulp fibers, that is, the fibers tend to flatten as moisture is withdrawn and to assume generally a ribbon shape; further, by the drying action the fibers of the fluff tend to withdraw from each other so that intimate contact required for cross-linking between fibers is not existent. Thus, the fibers are individually quite free to move and present increasingly large spacings between fibers as drying continues. The covered desiccator and contents were then placed in a forced air oven preheated to 150°C. The desiccator contents, while still covered, were heated to 130° within 30 to 40 minutes and then held at a temperature of 130-135°C. for 30 additional minutes to effect the cross-linking reaction. The desiccant present removed water formed during the reaction; the presence of water would materially slow the reaction and limit the extent to which reaction takes place. Thus, it is preferable to carry out the reaction under substantially anhydrous conditions. The resulting cross-linked fiber was then removed from the desiccator and washed over night in 0.3% aqueous ammonia solution to remove catalyst and unreacted formaldehyde as well as paraformaldehyde. Other dilute alkalis may be used for this purpose. The alkali wash was followed by thorough water washing and then air drying.

The apparent effect of the procedure of cross-linking in the loosely bonded state is to freeze the capillaries of the fluff and to set the fiber capillaries in

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partially closed condition such that the fibers remain set upon fiber rewetting.

A sample of the fiber product produced as described on hydrolysis with acid (12 Normal sulfuric acid for 2 hours at 90°C.), yielded 7% formaldehyde indicating the degree of cross-linking which had taken place. A sample of the fiber was also oven dried at 75°C. under reduced pressure for 24 hours, weighed, and then subjected to an atmosphere having 49% relative humidity at 73°F. The fiber in such atmosphere  
10 regained 5.0% moisture. This compares to a 7.0% regain for the untreated pulp when such was dried at 75°C. under the same conditions, and then subjected to the same humid atmosphere.

A half gram sample of the cross-linked fiber produced in accordance with the above procedure was dispersed in 200 milliliters of distilled water, and the resulting slurry was slowly poured into a cylindrical container having a screen bottom; the excess water was allowed to drain completely free from the fibers. By this action a wet pad of the fibers  
20 formed. The pulp pad was then subjected to progressively increasing loads in the cylinder. The load was applied by incremental weights on the piston of the cylinder, the piston bearing on the wet pad. The pad itself was allowed to drain free while each successive weight was applied. When drainage was completed for a given weight increment, the cylinder and its contents were weighed to determine the weight loss occasioned by each weight increment. A comparative test was run under the same conditions for the untreated pulp.

The comparative data set out in Table I presented  
30 hereinbefore indicate that the cross-linked pulp retained a

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considerably greater quantity of water under all conditions and particularly under positive pressure conditions ranging from 0.5 to 2 pounds per square inch. Such pressures are those which are encountered in sanitary napkin applications. As expressed in Table I, the water retention capacity of a mass of the cross-linked fibers produced in accordance with the invention is directly compared to the retention capacity of the original fibers in ratio terms. Thus, pulp produced in accordance with Example 1 retained 1.2 times by weight as much water when no external load was applied and about 1.8 times as much as at higher pressures.

The data of Table II show that a wet pad produced from the cross-linked pulp of Example 1 has a greater bulk and thickness under pressure than does a pad of similar fiber weight produced from the original fiber. Further, the thickness ratio at 0.5 psi is identical to the absorbent capacity ratio at the same pressure, and the thickness ratio is only very slightly below that of the absorbent capacity ratio for higher pressures.

#### Example 2

The same procedure was followed as in Example 1 except that the concentration of formaldehyde in the pre-saturating bath was 17.5% or approximately 1/2, while maintaining the same catalyst concentration, 0.5%. The formaldehyde yield of the cross-linked product, upon acid hydrolysis, was 6.9%. The moisture regained under the conditions as in Example 1 was 4.5%. Other pertinent data are shown in Tables I and II.

#### Example 3

The conditions of reaction were the same as in

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Example 1 except that the formaldehyde concentration during presaturation was 8.7% or approximately 1/2 that of Example 2. The formaldehyde yield of this pulp, upon acid hydrolysis, was 5.4%. The moisture regained was 4.4%. Other pertinent data are shown in Tables I and II.

Example 4

The procedure of Example 1 was followed except that the concentration of formaldehyde in the presaturating bath was reduced to 3.2% or slightly less than 1/2 of the Example 3 concentration. The formaldehyde yield of this pulp was 2.9%; the moisture regained 5.1%. See Tables I and II for other data.

Example 5

The reaction conditions were the same as in Example 1 except that reaction time at 130°C. was 60 minutes, making a total heating time of 90 minutes for the reaction. The formaldehyde yield of this pulp was 9.1%, the moisture regain 3%. Other pertinent data are set out in Tables I and II.

The rate of wicking for the material produced in accordance with conditions of this example was determined by the following test: a flat transparent plate 3"x3" received on a flat surface a batt of the fibers. The fiber batt had a dimension of 2 1/2"x4 1/2". The batt projected beyond one edge of the plate for approximately 1 1/2 inches and descended into a dye solution maintained in a trough. The level of the dye solution was held constant throughout the test. The time for the dye to wick from the one edge of the plate through the fiber to the remote end of the fiber batt was then measured. For the fibers of the example the time was 20 seconds. This compares with a wicking time of 49 seconds for control fibers; the



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control fibers were the untreated pulp fibers. Such control fiber is of the type customarily employed in commercial sanitary napkins.

Example 6

The reaction conditions were the same as in Example 1 except that reaction time at 130-135°C. was 90 minutes, making a total heating time of about 120 minutes for the reaction. The formaldehyde yield of this pulp upon acid hydrolysis was 9.7%; the moisture regain 3.0%. Other data are recorded in  
10 Tables I and II.

Although vacuum desiccator conditions employed in Examples 1 to 6 inclusive tend to increase the degree of reaction of the cellulose with formaldehyde at a given temperature and time, they are not essential. High absorbent capacity and bulk as well as reduced moisture regain may be achieved through reaction at atmospheric pressure.

Example 7

A 10 g. sample of unbeaten bleached southern pine kraft pulp was presaturated with formaldehyde and fluffed in  
20 the same manner as described in Example 1. The pulp was distributed on wire screens throughout a stainless steel box having the dimensions 10"x12"x13". The reaction box was equipped with a cover, thermometer, and vent tube. The box containing the presaturated pulp, barium oxide desiccant and paraformaldehyde was placed in a forced-air oven preheated to 140°C. The contents of the reactor reached 130°C. within about 15 minutes and were held between 130-135°C. for an additional 45 minutes, making a total reaction heating time of about 60 minutes. The pulp was then washed and dried  
30 according to the procedure of Example 1. The formaldehyde

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yield of this pulp was 5.5%; the moisture regain 3.4%. Absorbency data and wet bulk are given in Tables I and II.

Example 8

A sample of 100 g. of bleached kraft pulp was pre-saturated, as described in Example 2, that is, with formaldehyde concentration of 17.5%, and then fluffed. After air-drying, the fluff was placed in polyethylene bags for several days to inhibit formaldehyde loss; upon removal from the bags, the fluff was heated up to a reaction temperature of 130°C. in a 12 cubic ft. steam-heated forced-air oven. No paraformaldehyde and desiccant was employed in the oven. The fluff was maintained at about 130° for 30 minutes with air-recirculation, the large air volume serving to maintain any moisture present very low in concentration. After washing in 0.3% ammonia over the weekend and then with water, the cross-linked fiber was air-dried. The fiber had a formaldehyde yield upon hydrolysis of 4.6% and exhibited a moisture regain of 4.6% under the humidity conditions of Example 1. Absorbency and wet bulk are given in Tables I and II.

Graphs, Figs. 1 and 2, illustrate the relationship of the cross-linked pulp of the invention to pulp from which the cross-linked material is produced with respect to several important characteristics. The specific data of Figs. 1 and 2 is predicated upon pulp produced in accordance with Example 8. At higher cross-linking percentages, the disparity between the treated (cross-linked) and untreated pulp increases.

Fig. 1 indicates the filtration resistance of a mass of the cross-linked pulp compared with the filtration



resistance of an equivalent of the original pulp. As may be readily noted from Fig. 1, the filtration resistance of a mass of the cross-linked pulp is materially lower and changes less with applied pressure.

The procedure for obtaining the data of Fig. 1, which is a plot of specific filtration resistance against compacting pressure for the treated and untreated pulps, is based on the constant rate filtration method discussed in an article by R. P. Whitney, W. L. Ingmanson, and S. T. Han in TAPPI, Vol. 38, pages 157-166 (1955), and is as follows: a fiber sample is soaked in water for 6 hours and diluted to a consistency of 0.01%. This very dilute suspension is then filtered on a 150 mesh wire screen mounted in the open bottom of a 3-1/8" diameter Lucite cylinder. The volume rate of flow of the stock through the wire screen is maintained at a constant rate during the determination. As the pad of fibers builds up on the screen, so does the frictional drop across mat buildup. This continuously changing pressure is measured as a function of filtration time. The specific filtration resistance  $\mathcal{L}$  is related to the filtration time and pressure drop  $\Delta P$  by the formula:  $\theta = \frac{B \Delta P}{\mathcal{L}}$  where B is a parameter of the system and determined by the formula:

$$B = \frac{A^2 g_c}{\eta \omega \theta^2} ;$$

A is the mat area in square centimeters;  $g_c$  is 980 cm/sec<sup>-2</sup>;  $\eta$  is the viscosity of the slurry,  $\omega$  is consistency of the slurry, and  $\theta$  is the volume rate of flow.

In Fig. 2 the data clearly indicate the wide disparity in wet compressibility between the treated and untreated fibers. This compressibility is determined by subjecting the

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wet mat of fibers to external pressures by means of a permeable piston through which escaping water exudes under pressure. Weights are applied to the piston to effect loading while pad thickness is determined with a cathetometer. (TAPPI 35, No. 10 p. 439, 1952, Ingranson, W.L.)

As will be noted from Fig. 2, under the same compacting pressure the compressibility of the cross-linked pulp in the wet state is about one-half that of the untreated pulp. The compressibility is directly related to the pad concentration given in grams per cubic centimeter units. This compressibility change, believed occasioned by the cross-linking, is due to the wet stiffness or bending modulus change imparted to the fibers.

The data of Figs. 1 and 2 are a clear indication of the utility of the cross-linked pulp as filter media in many applications; and also particularly as cushioning and absorbent materials.

#### Example 9

A hand sheet sample containing about 20 g. of unbeaten bleached southern pine kraft pulp was presaturated as described in Example 2, that is, at a 17.5% concentration of formaldehyde. After air-drying to a moisture content of about 10%, the hand sheets were defibered in an experimental waste picker. The moisture retention aids this defibering action also. This defibering process affords a somewhat different mechanical action than the blender and requires use of no organic solvents. After defibering, the fiber was subjected to vacuum desiccation and the cross-linking process was also the same as described in Example 2. The cross-linked pulp was then washed over night in 0.5% NaOH and then thoroughly

with water and air dried. The formaldehyde yield of the pulp was 6.4%; the moisture regain 5.0%. Absorbency and wet bulk are given in Tables I and II.

Despite a variation of about 2:1 in the extent of cross-linking as illustrated by Examples 1 to 9 inclusive, the capacity to absorb water and pad wet thickness characteristics remain relatively constant (Tables I and II); while moisture regain varied somewhat, the greater degrees of cross-linking tended to result in lower regain. In the product of Example 10, the degree of cross-linking is materially less and the fiber characteristics indicate this.

#### Example 10

The procedure of Example 1 was followed except that no presaturating with formaldehyde occurred, but the catalyst only was introduced into the fiber by means of a bath, the catalyst being the same as in Example 1. After defibering the hand sheet to fluff form, the fiber fluff was initially introduced into a desiccator, dried down at reduced temperature over night under vacuum conditions and in the presence of solid paraformaldehyde and with barium oxide present as a desiccant. The resulting dry loose fluff, cross-linked under the conditions of Example 1, had a formaldehyde yield upon hydrolysis of 0.8%; the moisture regain was 5.4%. Absorbency and wet bulk data given in Tables I and II clearly indicate that the lower degree of reaction had an adverse effect upon these desirable properties of the cross-linked fiber.

Fig. 3 illustrates the contrast in dimensions of:  
a) a mat of untreated cellulose fiber which has been wetted, dewatered by centrifuging, and then dried; b) a mat of cross-linked material of the same fiber in two conditions, the fiber

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weights being the same in each of the three instances. In Fig. 3 the dry pad of cross-linked material has been subjected to identical wetting, centrifuging, and drying conditions as the untreated cellulose fiber. The wet pad of cross-linked material represents the condition upon removal from the centrifuge and the samples contained about 30% of moisture based on the weight of dry fiber. As will be readily noted, the cross-linked dry pad designated at 10 is nearly 6 times the axial dimension of the pad 12 of the original cellulose and the bulk of the wetted pad 14 in the cross-link state is materially greater than the bulk of pad 12. The pad 14, as illustrated, as already noted, contained by weight about 30 parts of water per 100 parts of fiber. It is further to be noted from the illustration that the cross-linked pad retains its general form in both the wet and dry state - in the present instance a cylindrical form.

The pad designated at 10 may be repeatedly compressed and released without material loss of resiliency, a factor which renders the cross-linked material useful in cushion applications. The wet bulk of pad 14 is a material element in the utility of the product fiber in absorbent applications.

The moisture regain and equilibrium moisture content of many fluffs is an important consideration both in manufacturing operations and in the storage of products embodying the fluff. Fluffs prepared in accordance with the following Examples 11 and 12 are compared as to the latter characteristic in Fig. 4 across the humidity scale. Other data appear in connection with the examples.

Example 11

30 Ten grams of bleached southern pine kraft fibers

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were formed into a hand sheet and the sheet was saturated with a 37% formaldehyde solution containing 0.5% aluminum sulfate as catalyst dissolved in the water. This sheet, after saturation, was blotted to about 200% wet pickup and then air-dried. The formaldehyde is deposited as paraformaldehyde within the fibers at this stage. The hand sheet, while still containing some moisture, was then dispersed as a fluff with the Waring blender in carbon tetrachloride and again quickly air-dried. Further drying took place under reduced pressure over barium oxide in the presence of formaldehyde for two days. While still under vacuum, the desiccator containing the pulp was heated in a forced-air oven at about 118°C. for a time period of 4 hours. Thereafter, the fiber was washed and dried as in Example 1. Such fiber provided the data for curve A in Fig. 4; the fiber also exhibited, upon hydrolysis, a yield of 9.8% indicating a somewhat greater degree of cross-linking. The moisture regain for the fiber was 3.1%, these results being comparable to data obtained in the method of Example 6. The hygroexpansivity of hand sheets of this fiber was about 1/3 of that of hand sheets of the untreated fiber.

#### Example 12

The conditions of Example 11 were repeated except the cross-linking reaction time was increased to 5 hours. The formaldehyde yield increased slightly to 10.9%, while moisture regain dropped to 2.8% and hygroexpansivity decreased further. The equilibrium moisture content at various humidities is designated by curve B in Fig. 4. Curve C in Fig. 4 designates the control pulp.

The centrifugal water retention of these latter two cross-linked pulps was approximately 1/4 that of the original

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untreated pulp, the per cent water retention decreasing from 88 to about 22. This measurement indicates the loss of affinity of the pulp for water upon cross-linking; this test employed an International clinical centrifuge Model CL operated at a speed of 4450 RPM and a relative centrifugal force of 2730 g. at the instrument septum (12.5 cm. radius). The time factor in each test was the same and about 15 minutes. Such test results were readily reproducible. The results attained with the equipment are equivalent to those attained by use of the procedure Thode, 10 Pergoni, and Unson described in TAPPI 43, No. 5, pages 505 to 512, May, 1960.

Example 13

A 20 g. sample of 1/4", 1.5 denier, high tenacity rayon was carefully dispersed in an aqueous slurry in a Waring blender. The slurry was dewatered to about 30% consistency to form a mat; this mat was then immersed in 200 mls. of 37% formaldehyde solution containing 5 grams per liter of aluminum sulfate. After thoroughly soaking and kneading in the formaldehyde solution, the pad was squeezed to a consistency of 24% 20 solids. The concentration of formaldehyde in the solution was reduced to 30% by the pickup of the fiber cake. After spreading out and air drying, the fibers were separated into a fluff in the Waring blender with carbon tetrachloride prior to cross-linking. The excess solvent was filtered off and the fiber again air dried free of carbon tetrachloride. Completion of drying was effected under reduced pressure at room temperature over barium oxide in the presence of paraformaldehyde.

The fiber, still under reduced pressure in a 30 vacuum desiccator, was placed in the forced-air oven at



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150°C., heated to 130° in 54 minutes and held at this temperature for 30 minutes. The fiber was steeped in 0.5% NaOH over night, washed thoroughly with water and air dried. The formaldehyde yield of the fiber was 13.7% and moisture regain 6.2%. The regain of the original rayon fiber was 11.2%. As in the instances of wood pulp fibers, the absorbent capacity of the treated rayon relative to untreated rayon was about 1.8 to 2 times while the relative wet thicknesses also had a ratio of about 2:1.

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#### Example 14

A 10 g. sample of bleached southern pine pulp in handsheet form was prepared for cross-linking with dimethylol urea. The dimethylol urea was initially dissolved in water at 60°C. to make a 5% solution which was then cooled. To 200 mls. of the cooled solution was added 0.5 g. of ammonium chloride (5% on the wt. of D.M.U.) as catalyst. The pulp sample as a handsheet was saturated with this solution, pressed to 200% wet pickup and air dried. The sheets were defibered in the blender with carbon tetrachloride, filtered and air dried again. The resulting fiber fluff was then heated to 132-135°C. in a forced-air oven for 30 minutes to effect cross-linking. The treated pulp was soaked in water over night and then washed thoroughly with water the following day and air dried.

20

Nitrogen analysis of the resulting pulp indicated that 9.4% had reacted with the fiber. The moisture regain under the conditions set forth in Example 1 was 5.5%. Absorbency and wet bulk were materially improved by the treatment but to a somewhat lesser degree than with formaldehyde for the same extent of cross-linking.

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In the treatment of the fibers in accordance with the invention, wood pulps respond to the treatment more readily than cotton but somewhat less readily than regenerated cellulose. The apparent explanation for this is the greater predominance of amorphous areas in the regenerated cellulose or rayon molecules in contrast to wood pulp and cotton. Also, with regenerated cellulose particularly, the fibers are not generally initially formed into a sheet but, upon drainage, clump together and are separable either in nonaqueous media with mild agitation or by strictly mechanical pickers - in either event the fibers contain moisture during the separation. The presence of some water in the mat or sheet during expansion of the mat or sheet to a fluff structure while mechanically separating is considered necessary to inhibit against fiber damage.

10 Sheets of wood fibers, saturated with the aqueous impregnant, tend to have a gelatinous appearance due to the ready tendency to take up the water; this is in contrast to the resultant cross-linked fibers wherein even when well wetted the fibers tend to be individually distinguishable to the eye.

20 Also, bleached wood fibers tend to respond more readily to the process of the invention than do the unbleached fibers. However, mats of the unbleached fibers are materially improved by the treatment of invention, particularly with respect to improved absorbency and wet bulk.

The reaction temperature is preferably relatively high to decrease reaction time. However, the temperature must obviously not be so high that the fiber is damaged. During the drying periods, preceding the cross-linking reaction, the temperature is suitably maintained low to inhibit

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loss of the impregnant by vaporization. With less volatile impregnants, this drying temperature may, of course, be higher but should not in any event be so high as to effect material cross-linking prior to fiber fluffing. The cross-linking reaction temperature should generally exceed  $110^{\circ}\text{C}$ . and, with wood pulp fibers, does not exceed about  $150^{\circ}\text{C}$ . Higher reaction temperatures eliminate the water formed during the reaction more quickly, which is desirable to prevent water pickup by and consequent swelling of the collapsed fibers.

- 10           Reaction time is related to the temperature, and the degree of cross-linking increases with time and temperature. However, relatively low degrees of cross-linking, as determined by acid extraction, are effective to produce the desirable fiber characteristics when the fibers have minimum contact during the cross-linking action. While the reaction time may be as low as 15 minutes and as high as several days, the minimum temperature should be at least about  $110^{\circ}\text{C}$ .; reactions carried out for a period of days at room temperature while producing products having lowered labiled water,
- 20   that is, water retention under a centrifugal action test, did not exhibit a lowered moisture regain or a lowered equilibrium moisture content property. In connection with moisture regain, it is to be noted that such tends to decline with extended time of cross-linking at higher temperatures (above  $110^{\circ}\text{C}$ .) even though the formaldehyde yield upon hydrolysis reaches a maximum; thus, in 2 to 3 hours of cross-linking reaction time, a maximum of cross-linking was achieved under a given impregnation condition; moisture regain continued to drop, however, when the cross-linking reaction
- 30   was carried to 4 and 5 hours.

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At low degrees of cross-linking, that is, about 2.2%, the interfiber bonding capacity is substantially eliminated and the capacity for imbibed water in a fluff of the cross-linked fibers under centrifugal action is about 1/2 or less than that of the untreated fibers. As the degree of cross-linking increases to 10 or 11%, the fibers have less tendency to hold water under centrifugal action, and the capacity is about 1/4 of that of the untreated fibers. In contrast, when cross-linking is effected in sheet form, with the fibers in close coherence, the fibers retain residual bonding capacity and show only a minor drop in imbibed water content and thus closely resemble the original untreated fibers.

Additionally, the product fibers demonstrate little affinity for dyes, which is contrary to the action achieved by cross-linking of fibers in the swollen state.

Sheets of paper formed with the cross-linked fibers and 20% by weight of ethyl cellulose as binder provide, upon drying, a porous open nap structure. Sheets in which the cross-linked fibers are present to the extent of 2-20% by weight with only untreated cellulose fibers provide an open porous structure from which the water is readily removed when drying; this factor, plus the resiliency imparted to a sheet by the cross-linked fibers, is important in papermaking machine operation, as the formed but wet sheet may be pressed hard to assist water removal but yet the sheet regains, after pressing, substantially the original thickness. In papermaking machine operation, the ability of the composite sheet to give up water under vacuum pressure and the ability to permit displacement of water by air pressure are further

Important factors in drying operations. This resistance to deformation and the high bulk (about 0.8 pounds per cubic foot to 1.2 pounds per cubic foot desirably) are of particular utility in filter papers. In Fig. 5 the numeral 16 designates cross-linked fibers in a sheet predominantly of normal cellulose fibers. When such a sheet as is illustrated in Fig. 5 includes a substantial but minor proportion by weight of the cross-linked fibers together with other untreated fibers such as wood pulp, cotton linters, and the like, the presence of the cross-linked fibers imparts to the sheet a materially increased void volume and materially increased resistance to fluid flow.

It will be understood that this invention is susceptible to modification in order to adapt to different usages and conditions and, accordingly, it is desired to comprehend such modifications within the invention as may fall within the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process of producing a cellulosic product which comprises impregnating a mass of substantially unbeaten cellulosic fibers of papermaking length with an aqueous solution containing a dissolved cross-linking agent and a dissolved catalyst for a cross-linking reaction between the cellulose and said agent, said impregnation causing said cellulosic fibers to be swollen and said agents and said catalyst to be taken up by the fibers; subsequently heating the fibers in dry form at cross-linking temperature; the improvement which comprises the combination of steps of, before heating to effect the cross-linking reaction, dewatering, drying, and expanding the mass of fibers without substantial cross-linking of the fibers to provide the fibers substantially free of water and so that cross-linking agent is retained in the fibers and the fibers are in the form of a loose dry fluff in which contact between individual fibers over any material portion of the length of the fibers is minimized and the impregnated fibers are themselves substantially non-swollen, flattened and collapsed whereby, upon cross-linking, the cross-linking reaction takes place primarily within the individual impregnated, non-swollen, flattened dry fibers of the fluff; and then heating the fibers in the dry fluff form at the cross-linking temperature to the extent that the individual fibers are materially stiffened and set in the substantially non-swollen, flattened condition and while in the said fluff form, said fibers being stiffened to an extent that they are reduced to powder if subjected to a refining operation in a papermaking process.

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2. In a process of producing a cellulosic product which comprises impregnating a mass of substantially unbeaten cellulosic wood pulp fibers with an aqueous solution containing a dissolved cross-linking agent and a dissolved catalyst for a cross-linking reaction between the cellulose and said agent, said impregnation causing said fibers to be swollen and said agent and said catalyst to be taken up by the fibers; the improvement which comprises the combination of steps of partially dewatering and drying said mass with attendant reduction in the cross-sectional area of the fibers of the mass, while the fibers are partially moistened expanding the mass of fibers without material damage to the fibers to the form of a loose fluffy mass to thereby minimize contact between fibers over any material portion of the length of individual fibers and to thereby limit a subsequent cross-linking reaction to substantially within fibers and substantially not between fibers, drying the fibers substantially free of water and so that cross-linking agent is retained in the fibers and without substantially advancing the cross-linking reaction but with further attendant reduction in the cross-sectional dimensions of the fibers and such that the resultant fibers are substantially non-swollen, flattened and collapsed, then heating the dry, flattened, impregnated wood fibers in the fluff form at a temperature of at least about 110°C. to cause cross-linking within the fibers to the extent that the individual fibers are materially stiffened and set in the substantially non-swollen, flattened condition and in the fluff form, said fibers being stiffened to such extent that subsequent refining in a conventional paper-making process would result in powdering of the fibers.

3. The process as claimed in Claim 1 and in which the cross-linking agent is formaldehyde and the cross-linking temperature is between about 110°C. and 150°C. and the time of heating at the cross-linking temperature is between about 15 minutes and five hours.

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4. The process of producing a cellulosic product which comprises impregnating a mass of unbeaten wood pulp cellulose fibers with an aqueous solution containing a dissolved cross-linking agent and a dissolved catalyst for the cross-linking reaction between the cellulose and said agent, removing fiber in mass form from the solution, partially dewatering and drying said mass with attendant reduction in the cross-sectional area of the fibers of the mass, while the fibers are partially wetted expanding the mass of fibers without material damage to the fibers to the form of a loose fluffy mass to thereby inhibit bonding between fibers over any material portion of the length of individual fibers to thereby limit a subsequent cross-linking reaction to substantially within fibers and substantially not between fibers, drying the fibers substantially free of water and so that cross-linking agent is retained in the fibers and without substantially advancing the cross-linking reaction but with further attendant reduction in the cross-sectional dimensions of the fibers and such that the resultant fibers are substantially non-swollen, flattened and collapsed, then heating the dried non-swollen flattened impregnated wood fibers in the fluff form at a temperature between about 110°C. and 150°C. to effect cross-linking within the individual fibers, heating the fibers at the said cross-linking temperature under conditions to inhibit moisture pickup by the fibers of the fluff during the reaction whereby the cross-linked fibers retain the collapsed form, said heating being effected to the extent that the fibers are set and materially stiffened such that refining in a conventional papermaking process would result in powdering of the fibers, thereafter washing the fibers, dispersing the washed fibers in water, and fabricating the dispersed fibers into a cellulosic article by water-laying and then drying, all without beating of the cross-linked fibers.



5. The process of producing a cellulosic fiber material which comprises the steps of impregnating unbeaten bleached cellulose wood pulp fibers in sheet form with an aqueous solution containing dimethylol urea as a cross-linking agent and containing a catalyst for the cross-linking reaction, removing the saturated sheet from the solution, partially dewatering the sheet, defiberizing the moisture containing sheet without causing material damage to the fibers to produce a loose fluffy mass of the fibers, drying the fluffy mass substantially free of water and so that cross-linking agent is retained in the fibers, and then effecting a cross-linking reaction by heating the loosely fluffed mass of dry fibers to a cross-linking temperature of at least about 110°C. in a volume flow of air for a time sufficient to cause cross-linking within the fibers to the extent that the fibers of the mass are materially stiffened and set, said fibers being stiffened to such extent that subsequent refining in a conventional papermaking process would cause destruction of the fiber to powder form.

6. Cross-linked cellulosic unbeaten wood pulp and in the form of a loose fluffy mass and characterized by internal cross-linking ether linkages between molecules of the cellulose, said fibers being wettable by and dispersible in but not substantially swollen by water, the said fibers forming the fluffy mass being stiff to an extent that the fibers are reduced to powder by refining operations in a papermaking process and these stiff fibers being in the fluffy mass only in minimal contact with each other over the length of the fibers so that interconnecting capillary voids are formed between the stiff fibers, said mass being capable of retaining from at least 1.2 to 2 times as much water and having a wet pad thickness of at least as much as 1.5 to 2 times the wet pad thickness of a corresponding mass of the untreated fibers from which the cross-linked fibers are derived, the said fluffy mass of cross-linked fibers being resiliently deformable in the dry and wet state.

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7. A heat set and water dispersible mass consisting essentially of cross-linked cellulosic fibers in the form of a loose fluff in which the fibers define capillaries, said fluff having a filtration resistance characteristic which is substantially constant over a compacting pressure range between 20 and 100 centimeters of water and a wet compressibility which is materially less than a fluff of non-cross-linked cellulosic fibers from which fibers the heat set mass of fibers is derived, said cross-linked cellulosic fibers of the loose fluff being stiff to an extent that the fibers would be reduced to powder by refining operations in a papermaking process.

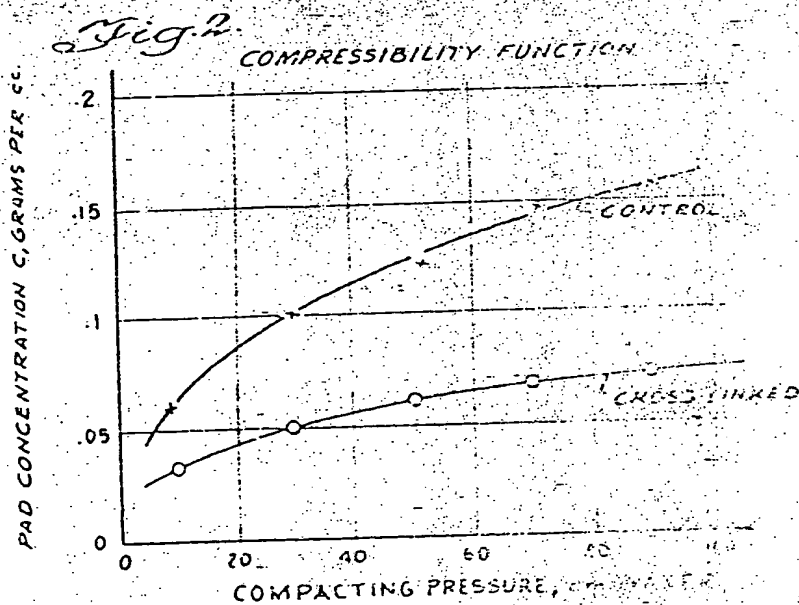
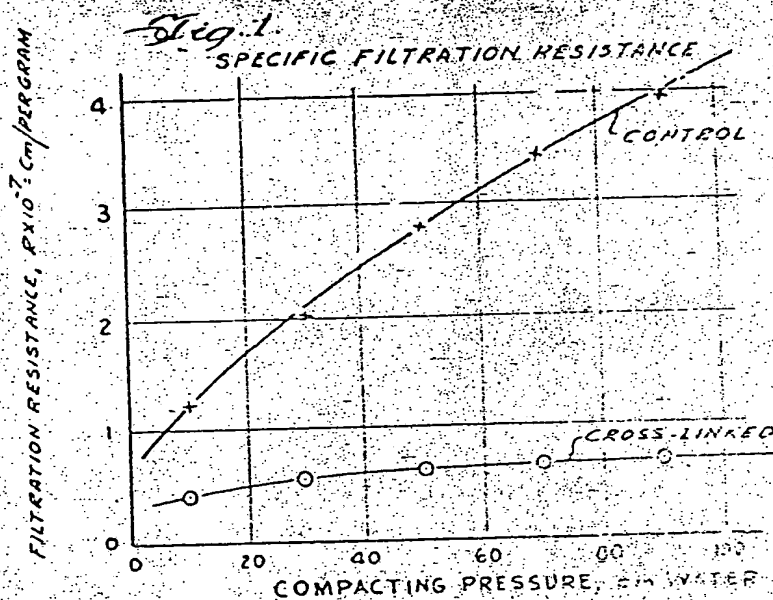
8. A water-laid product comprising between about 2 to 20% by weight of cross-linked cellulose fibers having little affinity for each other in the wet and the dry state and the balance of the fibers being essentially papermaking wood pulp fibers, the said cross-linked fibers being unbeaten and stiff to the extent that beating in a papermaking process reduces the fibers to powder, and said cross-linked fibers being distributed throughout said product and interrupting the natural bonding characteristics of the papermaking wood pulp fibers to the extent that the sheet is porous, readily wet pressed to release water, and resilient.



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## MANUFACTURE OF CELLULOSIC PRODUCT



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